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To cite this article: D V Ananchenko *et al* 2018 *J. Phys.: Conf. Ser.* **1115** 052027

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Luminescence of sapphire single crystals irradiated with high-power ion beams

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Abstract. Optical absorption, photo- and cathodoluminescence of a sapphire single crystal ($\alpha\text{-Al}_2\text{O}_3$) exposed to pulsed nanosecond radiation with high-power ion beams C^+/H^+ with an energy of 300 keV and energy density 0.5-1.5 J/cm² were first investigated in this work. It was found that under ion irradiation accompanied by heating of sapphire up to melting, the formation of F-type centers and their aggregates associated with oxygen vacancies was observed in the crystals under study. These centers have luminescence bands at 330, 410 and 500 nm which depend on the type and wavelength of the optical excitation. The appearance of a new PL emission at 435 nm, presumably associated with a complex vacancy-impurity defect, was also observed in the photoluminescence spectra.

1. Introduction

It is known that the luminescent properties of wide-band oxide dielectrics, in particular aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$, sapphire), are largely determined by the presence of active centers which are vacancies in various charge states in the anion sublattice [1]. The main types of anion defects in sapphire crystals are F^+ and F-centers which are oxygen vacancies that capture one and two electrons, respectively [2, 3]. There are two fundamentally different ways to create such defects: thermochemical and radiation coloring. In the case of thermochemical coloring, the crystals are subjected to heat treatment in an atmosphere containing vapors of metal [4] or carbon [5]. In addition to the diffusion of the metal into the crystal, oxygen diffuses from the crystal to the gaseous phase, this creates an oxygen deficiency in the anion sublattice of the crystal, i.e. anion vacancies. In accordance with the principle of charge compensation, oxygen vacancies capture one or two electrons forming electronic F^+ - and F-centers, respectively. Such centers are characterized by luminescence bands at 330 and 410 nm.

In the process of radiation coloring, crystals are irradiated with various types of corpuscular radiation, for example, neutrons [6], fast electrons [7], accelerated ions [8], protons [9]. To displace the atoms of the crystal lattice, the kinetic energy of the bombarding particles is required to be higher than the threshold energy of defect formation in the material under study. The energy of defect formation depends on the particle's mass and the nature of the irradiated material. Thus, the threshold energy of defect formation in aluminum oxide for electrons is about 400 keV [10]. Under radiation-induced colouring, defects are formed in oxide crystals following the impact mechanism [11], which explains a high radiation resistance of oxides.



A feature of oxide crystals which distinguishes them from alkali-halide crystals is the fact that when they are irradiated with X-ray or γ -radiation, the formation of new defects does not occur. Only the charge state of the defects existing in the source material before irradiation changes. In sapphire crystals with a high initial concentration of single anion defects, the formation of aggregate F-type centers at high doses of photon irradiation (about kGy) can also be observed [12].

A number of papers are concerned with the study of the effect of continuous bombardment with ions having energy about keV and MeV on the luminescence of sapphire crystals [13, 14]. At the same time there are almost no publications on the effect of high-power ion beams with nanosecond duration on sapphire luminescence. Such pulsed ion-beam treatment (PIBT) suggests irradiation of the sample with light ions (hydrogen, carbon, oxygen) with energy up to 300 keV during the nanosecond pulse ($\tau \sim 100$ ns). In this case, a large amount of energy ($W \sim 1$ J/cm²) is delivered to the sample, which leads to rapid heating of the near-surface layer of the sample to a depth of about 1 μ m, its melting and even evaporation. The outflow of heat into the crystal's bulk is accompanied by solidification of the formed melt [15]. Thus, PIBT is characterized with an intense thermal effect on the crystal, and its level of doping with light ions does not exceed 10^{13} cm⁻² per pulse. This treatment is close to pulsed laser annealing (PLA) which is widely used to modify the properties of near-surface layers. However, in the case of PIBT, unlike PLA, there is no loss of beam energy for reflection and this method of annealing is especially convenient to process optically transparent crystals. It should also be mentioned that the generation of high-power ion beams in an ion accelerator is accompanied by the generation of X-ray bremsstrahlung, which, as mentioned above, is able to change the charge state of defects in the irradiated crystal.

This work aims to study luminescence of the defects formed in sapphire both after rapid heating of its surface under the influence of PIBT, and when it is irradiated with concomitant X-ray bremsstrahlung.

2. Material and methods

Optically transparent samples of a single crystal of sapphire of c-orientation (c-Al₂O₃) with two-sided polishing and thickness of 2 mm («Monocrystal» company) were studied. The content of background impurities Ti and Cr, which are the most optically active in sapphire, did not exceed 0.5 ppm. PIBT of the samples was carried out by irradiation with a couple of pulses from ion accelerator TEMP. The ion beam contained $\sim 80\%$ of carbon (C⁺) and $\sim 20\%$ of hydrogen (H⁺) ions having the energy $E = 300$ keV. The pulse duration was $\tau \sim 100$ ns. The energy density of the ion beam was varied in the range $W = 0.5\text{--}1.5$ J/cm² by changing the distance between the sample and the beam focus (where the energy density of ion beam is maximal). PIBT with $W < 1.5$ J/cm² did not lead to visible changes of the samples, while PIBT with $W = 1.5$ J/cm² led to the appearance of disturbances on the surface of the samples. In another experiment, the sapphire crystals were located outside the ion beam zone, however in the region of action of X-ray bremsstrahlung. In this case, the samples were irradiated with a series of 10 pulses.

According to the calculations of SRIM program, the projective ranges (R_p) of C⁺ and H⁺ ions with energy 300 keV in Al₂O₃ are 0.44 and 1.7 μ m, respectively. Estimates of the thermal effect on sapphire during PIBT using the program developed by us [15] have shown that the threshold energy density for melting sapphire ($T_m = 2050^\circ\text{C}$) is $W = 0.5$ J/cm², and for its evaporation $W = 1.5$ J/cm². The melt depth reaches 0.8 μ m.

The optical absorption (OA) spectra were recorded using Lambda 35 (Perkin–Elmer) double beam UV–visible absorption spectrometer. Photoluminescence (PL) was recorded by the spectrometer LS-55 at room temperature. A xenon lamp with a power of 150 W, which works in a pulse mode was used to excite PL. The light emission was detected by R928 photomultiplier tube that has wavelength range from 200 to 900 nm and the maximal sensitivity at about 400 nm.

Pulsed cathodoluminescence (PCL) was excited at room temperature by a pulsed electron beam with a density of 60 A/cm², an energy of 130 keV, a pulse duration of 2 ns. As a source of electrons, a

pulse accelerator of RADAN type was used. PCL spectra were recorded in the range from 350 to 750 nm with spectral resolution of 2 nm.

3. Results and discussion

3.1. Optical absorption

Figure 1 shows OA spectra of the initial and ion-bombarded samples. It is seen that the ion-irradiated samples ($W=0.5$ - 1.5 J/cm², curves 2-5) have the absorption band of F-centers (205 nm) [1], which indicates the intensive generation of these centers in the samples under PIBT. With increasing energy density of the beam, an increase in the absorption coefficient at 205 nm is observed. The highest absorption coefficient is at the maximum energy density $W=1.5$ J/cm² (curve 5). The growth of OA at this energy density may also be due to some non-transparency of the sample as a result of reaching the boiling point of sapphire ($T_m=3000^\circ\text{C}$) according to calculations. The optical absorption spectrum of the samples irradiated with X-ray bremsstrahlung (curve 6) practically does not differ from the spectrum of the initial samples (curve 1). These measurements indicate that the formation of F-centers is a result of PIBT that generates oxygen vacancies by impact mechanism in the samples under study.

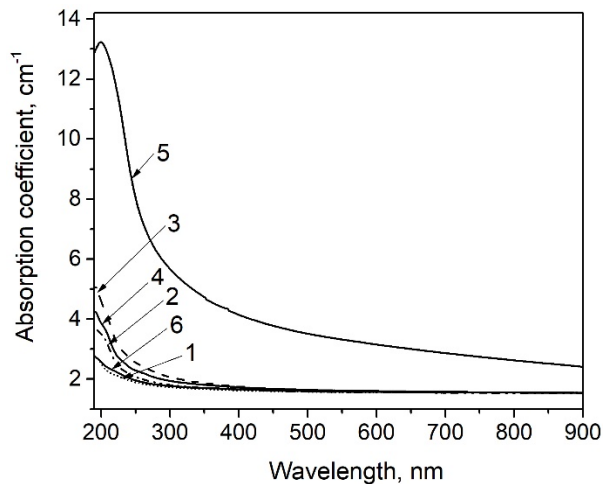


Figure 1. OA spectra of the initial Al_2O_3 ($W=0$, curve 1), and after PIBT with energy density $W=0.5$ J/cm² (curve 2), $W=0.8$ J/cm² (curve 3), $W=1.1$ J/cm² (curve 4), $W=1.5$ J/cm² (curve 5). The spectrum of the sample irradiated only with X-ray bremsstrahlung is also given (curve 6).

3.2. Cathodoluminescence

PCL also confirms high concentration of F-centers in the ion-irradiated samples (figure 2). The growth of energy density of ion beam leads to an increase in the intensity of PCL band at 410 nm associated with F-centers [2], that correlates with the results of OA measurement (figure 1). It is interesting that the luminescence band of F-centers is also observed in PCL spectra of the samples not exposed to PIBT (curve 1). This result indicates the presence of a certain number of F-centers in the initial samples, which may be due to the peculiarities of crystal growth. In addition, the formation of oxygen vacancies in the crystals not subjected to PIBT may be caused by a principle of charge compensation due to the existence of uncontrolled impurities in the initial crystals, the valence of which is less than the valence of aluminum. Thus, it is known that in crystals of aluminum oxide containing elevated concentrations of magnesium impurity (Mg^{2+}), a sufficiently high concentration of F-centers is observed [16].

Moreover, figure 2. shows that, in addition to the luminescence band of the F centers (410 nm), all the samples have luminescence with a maximum at 700 nm. The intensity of this emission varies slightly from sample to sample and does not correlate with the energy density of the ion beam. According to the literature data [17], PCL band at 700 nm can be associated with an impurity of trivalent titanium ion (Ti^{3+}), probably, introduced into the sapphire lattice during crystal growth. It is

known that titanium, even at trace concentrations, can significantly affect radiation-optical and luminescent properties of α - Al_2O_3 [18].

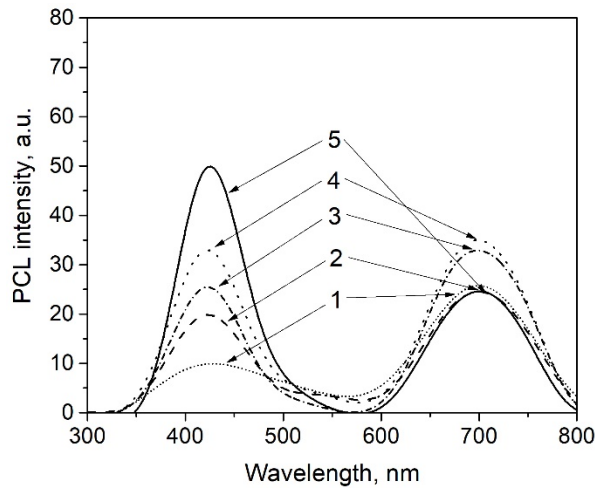


Figure 2. PCL spectra of initial Al_2O_3 ($W=0$, curve 1) and after PIBT with energy density $W=0.5 \text{ J/cm}^2$ (curve 2), $W=0.8 \text{ J/cm}^2$ (curve 3), $W=1.1 \text{ J/cm}^2$ (curve 4), $W=1.5 \text{ J/cm}^2$ (curve 5).

3.3. Photoluminescence

The excitation and emission spectra of the irradiated sapphire samples in the band of F-center (410 nm) are shown in figure 3. The highest intensity of F-centers emission is at $W=1.5 \text{ J/cm}^2$, which agrees with the results of OA measurements. PL excitation spectrum has a maximum at 214 nm, close to the maximum of optical absorption of F-center.

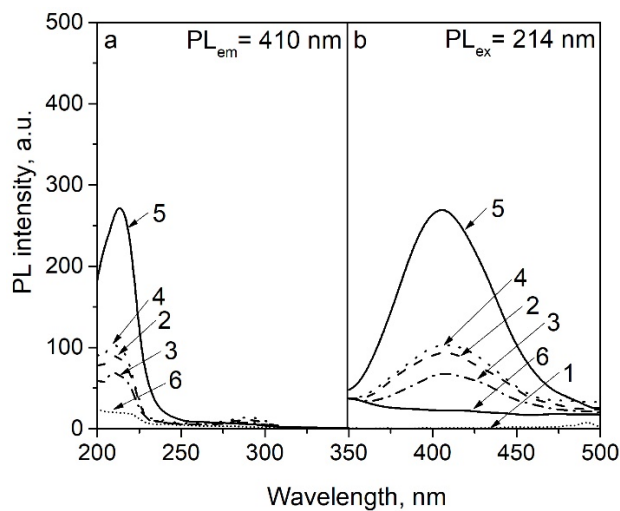


Figure 3. Excitation (a) and emission (b) spectra of PL of F-centers: initial Al_2O_3 ($W=0$, curve 1), after PIBT with energy density $W=0.5 \text{ J/cm}^2$ (curve 2), $W=0.8 \text{ J/cm}^2$ (curve 3), $W=1.1 \text{ J/cm}^2$ (curve 4) and $W=1.5 \text{ J/cm}^2$ (curve 5). The spectrum of the sample irradiated only with X-ray bremsstrahlung is also given (curve 6).

The excitation and emission spectra of PL of Al_2O_3 in the F^+ -centers are shown in figure 4. It can be seen that the excitation spectrum of these centers features two maximums at 238 and 267 nm, which agrees with the literature [3]. The most intense luminescence of the F^+ centers (330 nm) is observed in the samples irradiated with $W=1.1 \text{ J/cm}^2$ (curve 4). With an increase of W up to the maximum, the luminescence intensity at 330 nm drops substantially, which may indicate the formation of more complex centers containing oxygen vacancies.

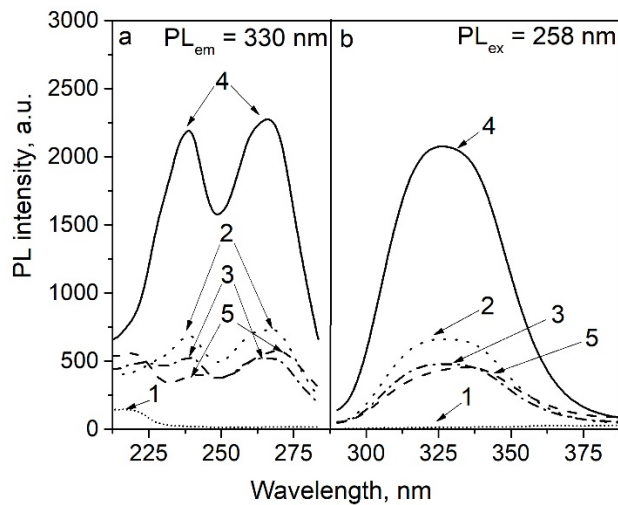


Figure 4. Excitation (a) and emission (b) spectra of PL of F^+ -centers: initial Al_2O_3 ($W=0$, curve 1), after PIBT with energy density $W=0.5$ J/cm² (curve 2), $W=0.8$ J/cm² (curve 3), $W=1.1$ J/cm² (curve 4) and $W=1.5$ J/cm² (curve 5).

A more detailed analysis of PL spectra shows that in the sapphire exposed to PIBT, along with single F and F^+ -centers, aggregate defects are also formed. Ion-irradiated samples excited with light of a wavelength of 300 nm have PL emission at 510 nm (figure 5), which may indicate the formation of aggregate F_2 -centers [1]. A nonmonotonic dependence of luminescence at 510 nm on the energy density of the ion beam was found. The maximum intensity is observed at $W=1.1$ J/cm². A similar nonmonotonic PL dependence of emission at 525 nm associated with aggregate F_2^{2+} centers on fluence was mentioned in [14] for nanocrystalline aluminum oxide irradiated with Au^{9+} (120 MeV) ions. PL intensity increase for fluence up to $1 \cdot 10^{12}$ ions/cm² due to increasing defect concentration caused by Au^{9+} ion irradiation. Further decrease of PL intensity at 525 nm was found, the authors attributed this to annihilation of the primary defects and growth of new defect centers.

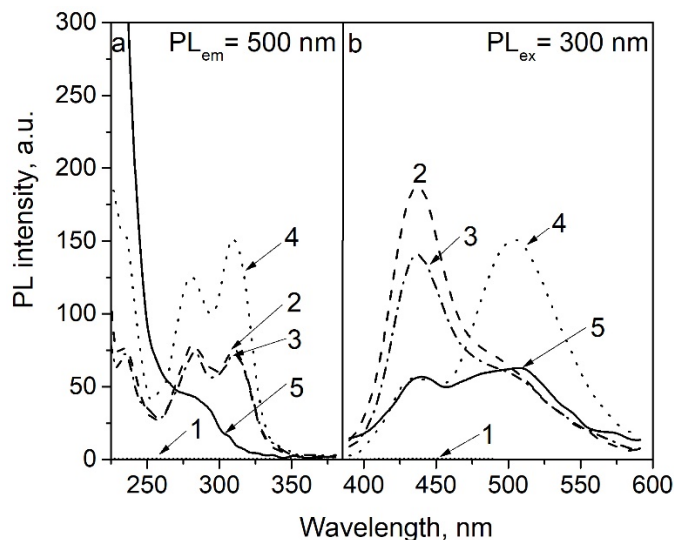


Figure 5. Excitation (a) and emission (b) spectra of PL of F_2 -centers: initial Al_2O_3 ($W=0$, curve 1), after PIBT with energy density $W=0.5$ J/cm² (curve 2), $W=0.8$ J/cm² (curve 3), $W=1.1$ J/cm² (curve 4) and $W=1.5$ J/cm² (curve 5).

A new interesting result of this work is the fact that in the PL spectra of all samples subjected to PIBT, there is a luminescence band at 435 nm (excitation at 300 nm) of unknown nature. Its intensity is maximum for the lowest energy density ($W=0.5$ J/cm², curve 2) and decreased with increasing of the energy density of the ion beam (figure 5b). The additional studies have shown that 435 nm emission has a maximum of the excitation at 280 nm that is close to the maximum excitation of the PL F_2 -centers. To associate this band with a specific type of defects in the sapphire crystals, additional research is required. There is a point of view that 435 nm (2.85 eV) emission of a sapphire crystal is

associated with isolated Ti^{4+} ions [19]. A close 430 nm emission in $\text{Al}_2\text{O}_3\text{:Ti}$ was identified as a result of charge transfer transition involving Ti^{4+} ion [20]. It is possible that titanium ions in the investigated crystals detected by PCL (figure 2) and oxygen vacancies form more complex defects (vacancy-impurity complexes) responsible for PL band at 435 nm.

4. Conclusion

Thus, the results of this work show that the irradiation of sapphire single crystal with high-power ion beams C^+/H^+ (energy of 300 keV) with the heating up to the melt phase causes intensive generation of F-type centers in them. This regularity follows from the results of OA, PCL, and PL investigation. Moreover, along with single F- and F^+ -centers, formation of more complex defects: aggregates of oxygen vacancies or vacancy-impurity complexes can be observed. The presence of the latter is a possible reason for the appearance of a new luminescence band at 435 nm with excitation at 280 nm in PL spectra of the irradiated samples. The nature and structure identification of the center responsible for 435 nm emission requires further investigations. The planned study of the thermoluminescent properties of the sapphire exposed to nanosecond irradiation of PIBT will reveal the possibility of its using for dosimetry of ionizing radiation.

Acknowledgment

The work was supported by the initiative scientific project № 16.5186.2017/8.9 of the Ministry of Education and Science of the Russian Federation. Experiments on ion irradiation of sapphire was done at the KIPT as a part of the state task.

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